

RAISING pH BY LOW-LEVEL AERATION FOR SOLUBLE PHOSPHORUS REMOVAL OF SWINE MANURE

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ABSTRACT. Soluble phosphorus (P) removal by increasing swine manure pH was investigated in this study. Sodium hydroxide (1 M) was used to increase the manure pH from 6.5 to 9. Two aeration treatments (intermittent and continuous) were also used to raise the manure pH from 6.5 to 8.0 (for the intermittent treatment) and from 6.5 to 8.4 (for the continuous treatment) in a period of 15 days. An airflow rate of 1 L/minute was used for both schemes. Results showed that raising the pH to 8 by sodium hydroxide (NaOH) led to a reduction in soluble P concentration by 80%. Increasing the pH above 8 had little effect on further removal of soluble P. For both the intermittent and continuous aeration programs, the manure pH increased by about 1 unit within the first day of experiment, accompanied by a 75% reduction in soluble P concentration in the liquid. The treatment with continuous aeration did not show advantage over the intermittent mode in removing soluble P from liquid swine manure. Therefore, to accomplish the same level of soluble P removal, intermittent aeration should be recommended to save energy.

Keywords. Soluble phosphorus removal, pH adjustment, Aeration, Swine manure.

Swine wastes containing nutrients such as nitrogen, phosphorus, and potassium at high concentrations have been used for fertilizer for years. In the last two decades, with the increased expansion and consolidation of the swine industry in the United States, it has become less possible to continue the traditional land disposal of excess swine manure without considering the potential environmental harm associated with this practice. Increasing concern has been voiced about potential pollution of surface and ground water by excess phosphorus resulting from the over-application of swine manure to cropland.

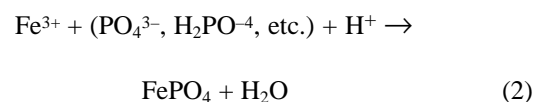
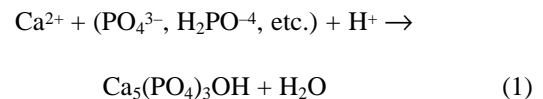
Processes that supply soluble P to the runoff water include: 1) desorption of P from soil particles, 2) release of P from chemical fertilizers, and 3) microbiological or physical (drying and freezing) release of P bound in organic materials such as humus, manure, and plant residues (Yli-Halla et al., 1995). Intensification and regional concentration of swine production has caused the overloading of manure in the land adjacent to the production sites. Since phosphorus is generally considered the limiting nutrient responsible for eutrophication, excess soluble P runoff from over-manured land to water bodies will provide this nutrient, thus resulting in the increased occurrence of blue-green algal blooms and other eutrophication problems in lakes and reservoirs (Kauppi et al., 1993).

Use of advanced techniques (chemical precipitation and biological processes) to remove P from wastewater is not a new topic, and tremendous work has been done to study these techniques for treating municipal and industrial wastewater (Joko, 1985; Marklund and Morling, 1994; Carlsson et al.,

1997; Kuba et al., 1997; Maurer and Boller, 1999). The techniques developed for such uses are relatively complex and costly, and thus are usually not suitable to swine producers. In recent years, several researchers have attempted to modify some of the advanced treatment techniques in order for them to fit into the waste management plan at farm level (Osada et al., 1991; Maekawa et al., 1995; Tilche et al., 1999). However, limited success has been reported because the modified techniques are still too expensive and require high maintenance.

These techniques were developed to produce effluent with a soluble P concentration less than 1 mg/kg, so the water can be used as drinking water for animals without causing health problems. However, under most circumstances, the treated liquid will be applied to cropland as fertilizer or soil amendment. The criterion for producing livestock drinking water is too stringent and entails unnecessary capital and operational expenses. As a matter of fact, as long as the soluble P concentration in the receiving land can be balanced to avoid significant runoff, low-level treatment, which could be inexpensive, may suffice to reduce the excess soluble P in swine manure before discharge. Unfortunately, to date, little information is available on the development of economically viable methods to remove soluble P from swine manure that are specially tailored to the needs and financial capabilities of swine producers.

The mechanism behind the removal of soluble P by pH adjustment is to form insoluble P compounds. According to Ripley (1974), the reactions between Ca and Fe and phosphates can be expressed as:



With increased pH (from 7 to 12), these compounds become stable and will not be hydrolyzed to release P into the

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solution. Therefore, it is often the practice in most industrial wastewater treatment plants that chemical compounds such as CaO, Ca(OH)₂, Al₂(SO₄)₃, and Fe₂(SO₄)₃ are added to the wastewater to form phosphate precipitates such as AlPO₄, Ca₅(PO₄)₃OH, and FePO₄ (Campbell et al., 1997), thereby reducing the P concentrations in the treated waste. However, this process, if used for treating swine manure, is not only expensive but also may cause secondary environmental pollution by raising the concentrations of chlorides and sulfates in the soil receiving the treated sludge (Kox, 1981). Since swine manure already contains certain amount of Ca and Fe that, under appropriate pH conditions, may react with soluble P to form insoluble compounds, removal of P by utilizing existing Ca and Fe in the manure without additional chemicals will certainly be of economic and environmental interest and deserves further research.

Raising manure pH can be achieved chemically, but it can also be done by aeration. In settled slurry, ammonia in solution is neutralized by dissolved CO₂ to form ammonium bicarbonate, which keeps the pH about neutral (Stevens and Cornforth, 1974). Passing an aerating gas mixture through the slurry purges CO₂ out of solution, and therefore causes the pH to rise. Extended aeration at a higher level may cause biological removal of phosphate, which also will result in a rise in pH (Fuhs and Chen, 1975).

Based on a laboratory-scale experiment, this article presents information regarding the removal of soluble P from swine manure by increasing pH using low-level aeration. For comparison, sodium hydroxide (NaOH) was used to raise the manure pH. Data from this study may reveal the possibility and feasibility of developing cost-effective treatment techniques for swine manure P management. Areas that need further research are also discussed.

MATERIALS AND METHODS

MANURE SOURCE

The manure used for the experiment was collected from a swine finishing building located at the University of Minnesota Southern Research and Outreach Center at Waseca, Minnesota. The building was equipped with a two-foot shallow pit with a pull-plug system. The manure was about two to three weeks old with 2.5% total solids content and an initial soluble phosphorus concentration was of 128 mg/kg. The pigs were fed on a regular corn/soybean diet.

pH ADJUSTMENT BY NaOH

Bench tests were carried out using eight 200 ml flasks, each containing 100 ml liquid swine manure. Sodium hydroxide (1 M) was added to each flask at ascending quantities from 1 to 8 ml in 1-ml increments. After adding NaOH, the flasks were gently shaken (not using a mixer to avoid possible aeration effects, which might contribute to the pH rise) to obtain a uniform solution and to enhance the chemical reactions between phosphates and Fe or Ca so precipitation could proceed. The pH of the manure samples in each flask was continuously monitored during the mixing process and recorded when the reading became stable for about 1 minute (with an accuracy of 0.001). The pH measurements were made using a pH/mV/ORP meter (Digi-Sense, Catalog No. P-05938-52, Cole-Parmer,

Vernon Hills, Illinois). After recording the pH for all the samples was finished, well-mixed samples from each flask were used for colorimetrically determining the soluble P concentrations as the phosphomolybdate complex after reduction with ascorbic acid by the standard methods (APHA, 1998) and a spectrophotometer (Hach, 1993). A raw manure sample was measured for both pH and soluble P as the control.

pH ADJUSTMENT BY AERATION

The experimental setup is shown in figure 1. Plexiglas tubes, 91.6 cm in height and 15.3 cm in diameter, were used as reactors. Each reactor was filled with liquid manure up to 84 cm, leaving a headspace of 7.5 cm. An air pump (Catalog No. 13-875-220, Fisher Scientific Company, Hanover Park, Illinois) provided air to each reactor at an airflow rate of 1 L/min, controlled by individual airflow meters mounted on each reactor. The air was introduced to the manure at 7.5 cm from the bottom of the reactor to maximize the travel distance and mixing effect. An airflow rate of 1 L/min was chosen to avoid creating a fully aerated environment in which the biological P removal process might become predominant, thus interfering with the planned research regarding the effect of pH on P removal.

Three treatments were studied: control, intermittent aeration, and continuous aeration. For the continuous aeration treatment, air was supplied to the reactors continuously throughout the test period. For the intermittent mode, aeration was controlled by a timer (Fisherbrand, Catalog No. 06-662-43, Fisher Scientific Company, Hanover Park, Illinois) that turned the air pump on and off at a two-hour interval. In other words, the aeration was programmed in such a way that the air pump was kept on for two hours and then kept off for the next two hours. A total of 9 reactors were used for the test, so measurements were made in triplicate for all the treatments. The room temperature was set at 22°C and the length of the test was 15 days.

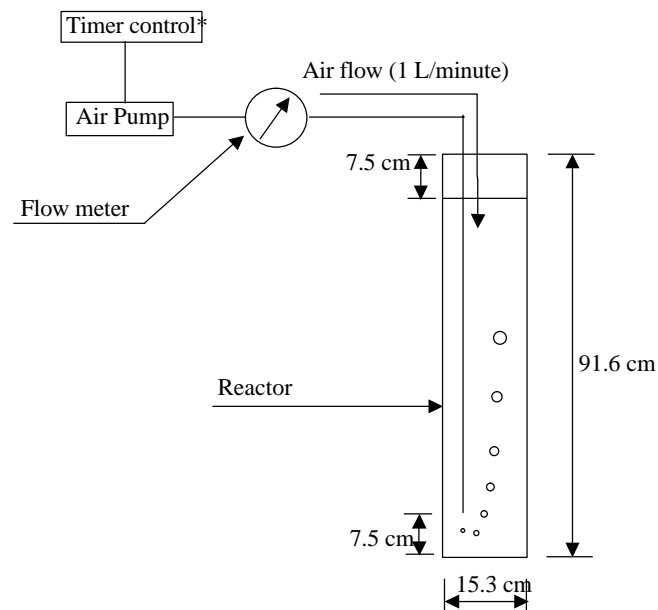


Figure 1. Schematic of experimental apparatus (*Timer used only for intermittent aeration).

The manure in each reactor was sampled and analyzed daily for total soluble P and pH. Samples of 100 mL each were collected from a point half way down from the surface during aeration. For the control, samples were taken during thorough agitation. The oxidation–reduction potential (ORP) was measured, also on a daily basis, directly from the manure in the reactors using the above mentioned pH/mV/ORP meter. A statistical *t*-test at a significance level of $P < 0.05$ was used for comparisons between treatments throughout the analysis.

RESULTS AND DISCUSSION

SOLUBLE P CHANGES BY pH ADJUSTMENT USING NaOH

Figure 2 shows the effect of pH on the soluble P concentrations in the manure. When pH increased from 6.5 to 9, the concentration of soluble P decreased from 130 mg/L to 10 mg/L (92% reduction). A quadratic relationship was fitted for P concentration with pH with a correlation coefficient of 0.983. According to the quadratic equation, an 80% reduction of total soluble P can be achieved if pH is raised to 8.

Past research showed that the reactions between phosphates and Ca or Fe are highly pH dependent (Moore and Miller, 1994). At a pH range of 4.7 to 7.1, iron will effectively react with soluble P to form iron phosphate precipitates. When pH is above 7.1 (with an optimum pH range of 7.2 to 12), calcium becomes the major reactant in the reactions for P removal. According to Campbell et al. (1997), swine manure contains much more calcium (110g/m³) than iron (6.6g/m³). Therefore, a great deal of P will be removed if pH moves towards the range in favor of the formation of calcium phosphate. The continuous removal of P over the pH range from 7 to 9 observed in this study was likely due to this mechanism.

It can also be seen from figure 2 that there were two pH ranges in which the rates of P reduction were apparently different. When pH increased from 6.5 to 8, the rate of P reduction observed was much greater than that when pH was above 8. Since the optimum pH for calcium can be up to 12,

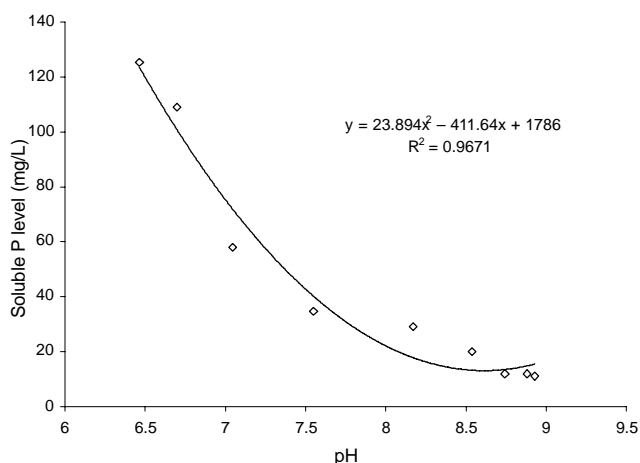


Figure 2. Changes in manure pH and soluble phosphorus concentrations due to the addition of sodium hydroxide.

the reduced rate could be due to the depletion of calcium in the manure, implying that further increase in pH might have little impact on P removal unless external calcium is added to the solution. Since the manure calcium was not measured in this study, this hypothesis cannot be verified. However, since little information is available in terms of reducing soluble P in wastewater by increasing pH alone without adding chemicals such as CaO, Ca(OH)₂, Al₂(SO₄)₃, and Fe₂(SO₄)₃, the findings in this study may provide impetus for further research on the utility of this method in treating diluted swine wastes for P removal.

SOLUBLE P CHANGES BY pH ADJUSTMENT USING AERATION

Variations of pH over the entire test period for the three treatments are presented in figure 3. For both the intermittent and continuous aeration treatments, the pH increased by about 1 unit to 7.5 on the first day and then increased gradually to 8.0 and 8.4, respectively, at the conclusion of the test. The pH of the control treatment remained nearly unchanged during the test period.

The effect of pH increase due to aeration on P removal is illustrated in figure 4, and the means and standard deviations of OPR vs. soluble P for different treatments are listed in table 1. When aeration started, the soluble P concentration in both aeration treatments dropped from 127 mg/kg to 31 mg/kg on the first day, with a rise of pH in the liquid manure from 6.5 to 7.5 and from 6.5 to 7.7, respectively. The sharp decreases of soluble P in the liquid for both cases were mainly due to the increase in pH. Examining the data presented in figures 2 and 3 and table 1 may support this statement. By entering pH values of 7.5 and 7.7 into the equation in figure 2 to calculate the P concentrations for both cases, the results are 43 mg/kg for the intermittent aeration and 33 mg/kg for the continuous aeration, respectively. These numbers were close to the numbers actually measured in the test, i.e., 31 mg/kg for the intermittent aeration and 32 mg/kg for the continuous aeration (table 1). The differences could be due to measurement errors. Therefore, it may be concluded that the soluble P reductions in the first day of aeration for both aeration schemes were caused by the pH rises.

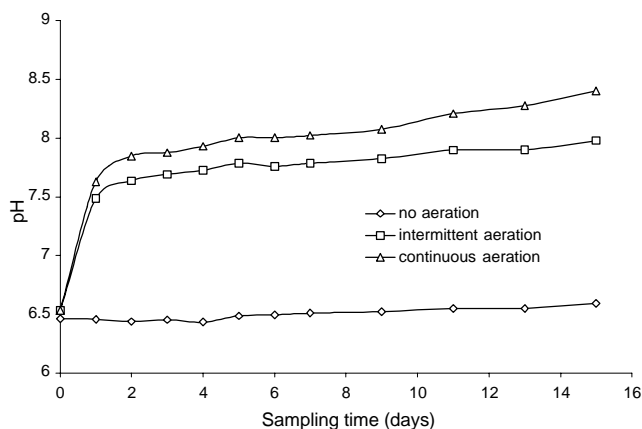


Figure 3. Changes in manure pH over time due to aeration.

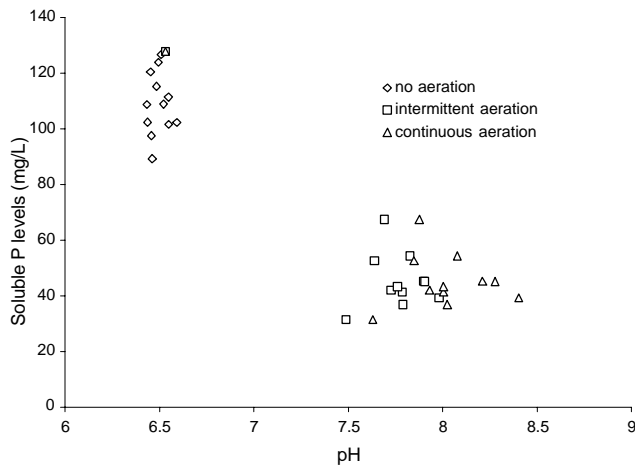


Figure 4. Variations of soluble P concentrations in the test manure vs. pH changes.

There are three possible mechanisms for pH increase due to aeration: phosphoric acid removal by aerobes, CO₂ purging, and ammonia production. Although there was theory on phosphoric acid removal from wastewater by the aerobes, which would accumulate it for polyphosphate synthesis, thus leading to a pH increase (Converti et al., 1995), the low ORPs in the manure (table 1) did not provide convincing evidence that these phosphate-accumulating aerobes could thrive to reach a significant population in order to be effectively functional. Neither would the time allow for biological activities to take place in order to produce ammonia, thus resulting in a pH rise, according to a study done by Beline et al. (1999) in which nitrification was observed after more than three days aeration at a much higher dissolved oxygen level than in the present study. Therefore, as indicated early, the large increase in pH observed in the

first day of study was primarily due to the purge of CO₂ out of the liquid manure (Stevens and Cornforth, 1974). With the aeration in progress, as the amount of oxygen in the air bubbling through the slurry increased, the increase in liquid manure pH may have been due in part to an increased rate of organic matter degradation, which resulted in increased ammonia production. Therefore, the maintained high pH levels after the first day of aeration may result from the combination of the above-discussed mechanisms.

Aeration significantly increased the ORPs of the treated liquid manure, as compared to the control (table 1). For the control, although there were some significant differences ($P < 0.05$) in ORP on a day-to-day basis due to small standard deviations, the average value was around -330 mV. For the two aeration treatments, the ORPs reached their highest levels in the first day and decreased gradually in the succeeding days. In spite of the decreases, they still remained statistically higher than the control throughout the test period. However, it has to be recognized that, although the ORPs were significantly enhanced by the aeration treatments, the aeration level is still considered low as defined by Burton (1992).

It is interesting to note that starting from day 5, there was a tendency for the ORPs in the continuous aeration treatment to become significantly more negative than those in the intermittent aeration mode. The reason for this observation is unknown. By definition, ORP represents the oxidation-reduction power of the solution. Thus, less negative ORP means high oxidizing but low reducing potential. The data in this study appeared to show that intermittent aeration would provide more oxidizing potential to the solution than continuous aeration with the same aerator, which seemed impossible. Further research is needed to gather more information to verify this finding.

Table 1. Means and standard deviations of ORP and soluble P during the 15-day test period for different treatments^[a].

Sampling Days	ORP (mV) No Aeration	ORP (mV) Intermittent Aeration	ORP (mV) Continuous Aeration	P (mg/L) No Aeration	P (mg/L) Intermittent Aeration	P (mg/L) Continuous Aeration
0	$-334 \pm 3.5^{a,x,z,v}$	$-317 \pm 3.5^{b,x}$	$-315 \pm 0.6^{b,x}$	$115.6 \pm 0.0^{A,X}$	$127.8 \pm 20.8^{A,X}$	$127.8 \pm 6.5^{A,X}$
1	$-326 \pm 8.1^{a,x,y,z}$	$-176 \pm 3.5^{b,y}$	$-172 \pm 2.1^{b,y}$	$122.9 \pm 10.6^{A,X}$	$30.9 \pm 6.1^{B,Y}$	$31.5 \pm 2.3^{B,Y}$
2	$-330 \pm 1.5^{a,x}$	$-199 \pm 1.7^{b,z}$	$-181 \pm 3.2^{c,z}$	$129.3 \pm 5.5^{A,X}$	$58.4 \pm 7.5^{B,Z}$	$52.6 \pm 9.1^{B,Z,V}$
3	$-329 \pm 3.2^{a,x,y,z}$	$-290 \pm 10.6^{b,v,u,s}$	$-306 \pm 8.7^{b,x,w,s}$	$124.5 \pm 11.8^{A,X}$	$48.0 \pm 7.3^{B,Z,V}$	$67.4 \pm 18.4^{B,Z}$
4	$-329 \pm 1.0^{a,x}$	$-282 \pm 4.0^{b,v,t}$	$-300 \pm 0.6^{c,w}$	$123.2 \pm 6.6^{A,X}$	$38.2 \pm 6.3^{B,Y,V}$	$42.0 \pm 3.4^{B,V,T}$
5	$-324 \pm 1.7^{a,y}$	$-260 \pm 3.8^{b,w}$	$-293 \pm 11.0^{c,w,v,s}$	$102.1 \pm 15.8^{A,X}$	$42.8 \pm 3.7^{B,Y}$	$41.3 \pm 4.4^{B,V,W,T}$
6	$-327 \pm 1.5^{a,x,y}$	$-285 \pm 1.7^{b,v}$	$-297 \pm 1.5^{c,w}$	$110.7 \pm 10.6^{A,X}$	$41.9 \pm 2.2^{B,Y,V}$	$43.3 \pm 3.8^{B,V,T}$
7	$-331 \pm 2.1^{a,x,z}$	$-275 \pm 6.1^{b,t}$	$-289 \pm 0.6^{c,v}$	$109.2 \pm 7.2^{A,X}$	$52.3 \pm 3.5^{B,Z}$	$36.8 \pm 1.4^{C,W,T}$
9	$-333 \pm 0.6^{a,z}$	$-300 \pm 2.0^{b,u}$	$-298 \pm 3.1^{b,w}$	$93.6 \pm 3.2^{A,Y}$	$37.3 \pm 3.3^{B,Y,V}$	$54.3 \pm 16.4^{B,Z,V,W,T}$
11	$-334 \pm 1.2^{a,z}$	$-283 \pm 2.5^{b,v}$	$-300 \pm 2.6^{c,w}$	$102.1 \pm 16.1^{A,X,Y}$	$36.1 \pm 2.1^{B,Y}$	$45.3 \pm 0.3^{C,V}$
13	$-335 \pm 0.6^{a,z}$	$-288 \pm 7.6^{b,v,t,s}$	$-318 \pm 6.0^{c,x,s}$	$89.3 \pm 6.2^{A,Y}$	$45.5 \pm 8.4^{B,Y,Z}$	$45.1 \pm 3.4^{B,V}$
15	$-337 \pm 1.1^{a,v}$	$-294 \pm 5.6^{b,s}$	$-321 \pm 6.5^{c,x,s}$	$112.1 \pm 7.3^{A,X}$	$36.1 \pm 3.4^{B,Y}$	$39.3 \pm 1.2^{B,W,T}$

^[a] Lowercase letters (a, b, c, x, y, z, u, v, w, s, t) are used for ORP comparisons, while uppercase letters (A, B, C, X, Y, Z, U, V, W, S, T) are for P comparisons. Different letters (a, b, c, A, B, C, etc.) indicate statistically significant differences between columns in the same row, while letters x, y, z, u, v, w, s, and t indicate statistically significant differences between rows in the same column. Student's *t*-test was used for the comparisons at a significance level of $P < 0.05$.

According to table 1, there was no significant difference in terms of P concentration for the treatment without aeration during the course of the test. In contrast, statistically significant reductions in soluble P concentrations were revealed by data following day 1 for the two treatments with aeration. The data also showed that although there were small fluctuations in P concentrations in the aerated manure on a day-to-day basis, further reduction of P was not observed, suggesting that extended aeration beyond one day may be unnecessary if removal of P is the main purpose of the treatment. In addition, the continuous aeration treatment did not show an advantage over the intermittent aeration for soluble P removal, indicating that it could be possible to reduce the energy consumption by 50% while still accomplishing the same reduction of soluble P concentration.

Another interesting observation concerned the relationship between ORPs and P concentrations for the two aeration treatments. Starting from the second day, although the ORPs started to become more negative, the P concentrations in the treated liquid manure did not rebound significantly ($P < 0.05$). This means that no new soluble phosphorus was generated in the liquid as the aeration continued. Since the pH was maintained at a higher level for both treatments in the test period, the reverse reactions leading to the release of phosphorus from the insoluble precipitates could hardly take place. Therefore, it may be inferred that the production of soluble P from another source, i.e., biological release, was also tempered under the set environment. It is known that soluble P concentration in the solution will increase under anaerobic conditions as a result of increased breakdown by microbes of the stored polyphosphates in the cell for energy generation. The results from this study therefore indicated that providing low-level aeration to liquid manure could impede this process. Charpentier et al. (1987) proposed that when the wastewater ORP was maintained at a level above -300 mV, the soluble P would be trapped in the sludge and would not be released into the liquid. This proposal was apparently confirmed by the data in this study. The findings also imply that if manure is not planned to be spread immediately after aeration treatment, it is important to maintain low-level aeration to prevent the ORP from falling below -300 mV, thus minimizing the biological phosphorus release during the storage time.

SUMMARY AND CONCLUSION

1. Raising pH alone to increase the formation of insoluble phosphate compounds can reduce swine manure soluble phosphorus. Without using external chemicals to assist precipitation, a rise in pH to 8 can achieve a reduction in soluble P concentration by 80%. Further increase in pH beyond 8 appeared to have little impact on P removal. This could be due to the depletion of reactants such as Ca and Fe in the liquid manure, thus reducing the precipitation rate. More data is needed to verify this assumption.
2. The manure pH can also be raised by low-level aeration. For both the intermittent and continuous aeration treatments, the manure pH increased by about 1 unit within the first day of operation, accompanied by a 75% reduction in soluble P concentration. According to this study, continuous

aeration did not show advantage over intermittent aeration in removing soluble P from liquid swine manure. Therefore, using intermittent aeration can reduce energy consumption by 50%, as compared to continuous aeration.

3. The information presented in this paper has indicated the possibility of effectively reducing soluble P concentration in liquid swine manure at a potentially reduced cost. With this information, further research should be directed to the development of a simple (could be portable) aeration system that can be applied to current manure storage to provide minimum aeration for a short period of time for P removal. The liquid portion of the treated manure that contains low soluble P should be spread immediately after the treatment, and the solid portion should be processed separately. In this way, the environmental concerns about P pollution due to swine production may be ameliorated.

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